PREPARATION OF BENZOPOLYTHIA COMPOUNDS AS TWO-DIMENSIONALLY EXPANDED POLYTHIA SYSTEMS AND THE ESR SPECTRA OF THE RELATED COMPOUNDS

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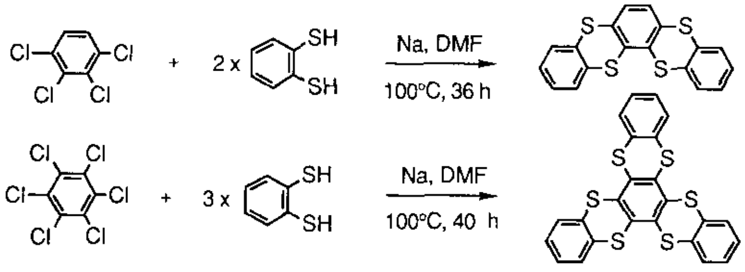
Abstract- Benzopolythia compounds, dibenzo-1,4,5,8-tetrathiaphenanthrene and tribenzo-1,4,5,8,9,12-hexathiatriphenylene, have been prepared. The esr spectra of cation radicals of several polythia compounds reveal delocalization of spin density at the sulfur atoms by the aromatic or olefinic moieties.

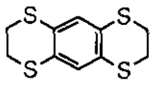
In sulfur chemistry a polythia-aromatic compound has received considerable attention because of its versatile properties as a mono or a poly cation radical.[1] Recently we have found novel properties of polythia compounds bearing ethylenedithio groups.[2, 3] Formation of the very stable cation radicals and the charge transfer complexes with electron acceptors, such as TCNQ, was ascertained spectroscopically (e.g. esr, ir) as well as by elemental analysis.[2, 3] This fact may open a way to new families of electron donors in organic conductors and organic ferromagnets.[4 - 8] We report here preparation of benzo derivatives of 2,3,6,7-tetrahydro-1,4,5,8-tetrathiaphenanthrene (HTP) and 2,3,6,7,10,11-hexahydro-1,4,5,8,9,12-hexathiatriphenylene (HTT). The benzo substituents are expected to delocalize spin density of the cation radicals and to enlarge stacking interaction between the donors and some acceptors in a fashion expanded two-dimensionally, giving the stable CT complexes.

Scheme

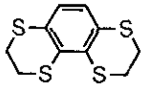


BTP
1.4%

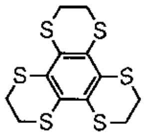
BTT
4.0%



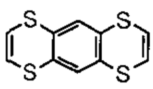
HTA



HTP



HTT



TA

Dibenzo-1,4,5,8-tetrathiaphenanthrene (BTP) and tribenzo-1,4,5,8,9,12-hexathiatriphenylene (BTT) were synthesized as shown in Scheme. Sodium was dissolved into a solution of o-benzenedithiol in dry DMF.[2] 1,2,3,4-Tetrachlorobenzene or hexachlorobenzene was added into the mixture and heated at 100°C under nitrogen. The crude product was purified by silica gel column chromatography and preparative hplc[9] repeatedly, affording extra pure BTP(1.4%) or BTT(4.0%). The structures were unambiguously identified by 500 MHz ^{1}H, 125 MHz ^{13}C nmr, and mass spectra.[10] The esr spectra of BTP, BTT and the related compounds were easily measured in $AlCl_3$-CH_2Cl_2 or $AlCl_3$-CH_3NO_2, indicating generation of the stable cation radicals. BTP, BTA and tetrathiaanthracene (TA)[2] having double bonds show smaller g values (2.0080, 2.0080, 2.0081, respectively) than HTT, HTP, and 2,3,6,7-tetrahydro-1,4,5,8-tetrathiaanthracene, HTA, (2.0086, 2.0083,[3] and 2.0082,[3] respectively). These results clearly indicate that spin density of sulfur atoms in the radicals of BTP, BTT, or TA was reduced by π-electrons of aromatic or olefinic moieties. Among the polythia compounds, HTA and HTP afforded well-resolved esr spectra in CH_3NO_2-$AlCl_3$ system. The quantitative computer analysis of hyperfine structure of these spectra between 10 and -60°C by the use of the modified Bloch equations[11] indicates that there is quite an interesting dynamic behavior of the cation radicals, that is, conformational interconversion between axial and equatorial positions for the ethylenedithio protons. The activation energies thus estimated in the interconversion for HTA and HTP are 2.7 and 3.4 kcal/mol, respectively.

We are currently going on the detailed esr study of BTP, BTT, and TA and the MO calculation of the cation radicals.

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9. Performed on Japan Analytical Industry LC-09 instrument with JAIGEL-1H column (20 mmϕ x 600 mm x 2) and $CHCl_3$ as an eluent.
10. BTP; ^{1}H nmr ($CDCl_3$) δ 7.23-7.28(m, 4H), 7.33(s, 2H), 7.44-7.48(m, 2H), 7.57-7.61(m, 2H), ^{13}C nmr ($CDCl_3$) δ 127.39, 127.69, 128.14, 128.53, 129.22, 134.78, 134.99, 135.44, 136.03; ms(m/z) 354(M^+); mp 180.5-181.5 °C. BTT; ^{1}H nmr ($CDCl_3$) δ 7.27-7.31(m, 6H), 7.56-7.61(m, 6H), ^{13}C nmr ($CDCl_3$) δ 128.35, 129.13, 134.76, 135.07; ms(m/z) 492(M^+); mp >300 °C.
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